

## ELECTRON DENSITY IN GRAPHENE LAYERS: IMPLICATIONS FOR CARBON REACTIVITY

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### INTRODUCTION

Much has been accomplished in the last few decades to eliminate empiricism from the kinetic treatments of the combustion and gasification of coals, carbons and graphite (1). However, our ability to further quantify the important details of carbon reactivity is now at a critical juncture from both the experimental and the theoretical point of view. The experimental determination of active and reactive surface areas -- typically straightforward but sometimes tedious and complicated by stringent accuracy requirements -- does lead to satisfactory predictions of reactivity as a function of both carbon nature and carbon burnoff. Although not many such results are available in the literature, they do lend support to recent predictions (2,3) that the turnover frequency at the free carbon sites may be burnoff-dependent. In other words, it is not sufficient to know the carbon's total, active and reactive surface areas to understand all the important details of its reactivity behavior; the rate constant normalized with respect to the reactive area may be burnoff-dependent because the dynamics of surface coverage affect not only the number of sites but also their reactivity (3). In such circumstances, experimental complications increase further and mapping the intrinsic reactivity against the important variables (heat-treatment temperature, reaction temperature, pressure, extent of burnoff) remains quite a challenge.

On the other hand, while the *ab initio* molecular modeling of chemical reactions (4) has become possible and is now widely practiced, the extrapolation from either graphite or polyaromatic hydrocarbons to the carbons of interest (e.g., coal chars) is still subject to much uncertainty. In a recent study, Chen and Yang (5) presented a systematic procedure for selecting a suitable calculation level and model structure for the application of the *ab initio* method to the graphite system. They concluded that the use of B3LYP/6-31G(d) model chemistry for molecular properties and of HF/3-21G(d) for stability and geometry optimization, using a seven-ring graphene layer, is the most suitable compromise between accuracy, relevance and computational cost. Thus, for example, they used this approach, coupled with the atoms-in-molecule method (see below), to arrive at the intuitively appealing (and obvious!?) conclusion that a relatively large negative charge exists on the "unbalanced graphite edge sites" which are the "[re]active sites for carbon gasification reactions."

Before attempting to theoretically analyze the interaction between a gaseous molecule ( $O_2$ , NO,  $CO_2$ ,  $H_2O$ ) and the carbon surface (6), it is useful -- and indeed probably necessary -- to evaluate the theory in terms of its consistency with some well known facts about the electronic structure and surface chemistry of graphene layers. At the same time, it is expected that such a theoretical analysis will clarify the details of this electronic structure and thus help in the quantification of gasification reactivity. In particular, the electron density at the edge sites and its changes with the concentration of heteroatoms is of immediate interest. The affinity of the carbon surface for an oxidizing gas is assumed to be dependent on this electron density at the free carbon sites.

The electron density of a molecule is a fundamental property in quantum chemistry, readily amenable to theoretical analysis. The classical Mulliken population analysis, which assigns atomic charges, though arbitrary, is implemented in most commercially available molecular modeling programs. Its results should be viewed with caution, however, because they are known to be dependent on the level of theory and the basis set used. In contrast, the more recent atoms-in-molecule (AIM) approach is claimed not to have this limitation.

In this study a comparison is thus made between the Mulliken population analysis and the AIM approach in their ability to evaluate the electron densities in graphene layers by considering 1-, 2- and 4-ring aromatics. Following the pioneering work of Coulson and coworkers (7), "we can, provisionally, neglect all inter-layer effects and consider only the single layers separately."

## COMPUTATIONAL METHODS AND MODEL STRUCTURES

The Gaussian 98W software package (4,8) was used in most calculations. When deemed necessary, it was complemented by Hückel molecular orbital as well as semi-empirical analyses. Figure 1 summarizes the structures that were selected for closer scrutiny. Their selection is based on the following considerations. We agree with Chen and Yang (5) that saturation of the boundaries of these model structures is a crucial step in reactivity calculations for graphite and, especially so, for carbons whose crystallites are much smaller than those in graphite. However, the choice of free edge sites versus hydrogen-saturated sites should not be one of convenience (7); rather, it should attempt to reflect the by now well documented delicate balance between free sites, H-saturated sites and oxygen-saturated sites (9). A comparison of bond orders and charge distributions in structures 1-4 within each series will thus be of interest. Similarly, ever since the pioneering work of Coulson and coworkers (7,10), as well as that of Stein and Brown (11), it has been clear that the size of the graphene layer is an important variable to consider even when edge chemistry is of primary interest. More recent theoretical analyses of carbon gasification (2,3), as well as experimental studies of liquid-phase adsorption on carbons (9), have indeed suggested that the electron density in the basal plane of the graphene layer is affected in an important way by the presence of heteroatoms at the edges, and vice versa. It is thus necessary to assess the dependence of these electronic effects on the size of the graphene layers. A comparison of the bond orders and charge distributions in series B1-N1-P1, B2-N2a-P2a, B3-N3a-N3b-P3a-P3b-P3c, B4-N4a-N4b-P4a-P4b-P4c will make this possible in a first approximation. An additional benefit of analyzing model structures containing few rings is that the results (model structures B1, B3, N1, N3a, N3b, P1, P3a, P3b and P3c) can be readily compared with experiments. Since some "50 carbon atoms" which form a "condensed system with at least two, and preferably three, hexagons in each direction" (7) are thought to be necessary before the model system "may be regarded as graphite and not as a large molecule approximating to graphite" (7), in future work we shall analyze even larger heteroatom-containing graphene layers. For now, we focus on the electron density at the edge carbon atoms, since surprisingly few papers (12,13) have been devoted to this crucial issue for carbon gasification reactivity.

## PRELIMINARY RESULTS AND DISCUSSION

Tables 1 and 2 summarize some of our preliminary results. A key unresolved issues is the degree of localization of carbon's  $\pi$  electrons during gasification reactions. In particular, if the localization of  $\pi$  electrons contributes to the stabilization of free edge sites, as has been argued elsewhere (9), then the resultant redistribution of charge density will produce changes in C-C bond lengths, thus affecting CO and/or CO<sub>2</sub> desorption, as well as changes in the affinity of edge sites toward reactant gas chemisorption. Indeed, Wiberg (14) recently used ab initio MO theory to conclude that  $\pi$  electron distribution in condensed aromatic systems is the dominant factor in determining bond lengths.

It is seen in Tables 1a and 2a (note the underlined values) that the presence of carbonyl oxygen produces a consistent increase in the C-C bond lengths adjacent to the C=O group. This in turn supports the concept of induced heterogeneity in carbon gasification kinetics (2,3). It is also interesting to note that the predicted adjacent bond weakening effects of chemisorbed oxygen are sensitive to both the concentration and the exact location of C-O surface complexes. Thus, for example, while bond C8-C9 in structure P3b is weaker than bond C9-C12, as intuitively expected, bond C6-C7 in structure P3a is not weaker than bond C7-C14.

Tables 1b and 2b show that the electron density distribution using the Mulliken population analysis must be subjected to close scrutiny. (The underlined values in Table 2b are the atomic charges on the edge carbon atoms.) While the C atoms adjacent to the carbonyl group are predicted to have a higher affinity for O<sub>2</sub>, the electron density at other reactive sites may be lower.

To what extent these trends are affected, in quantitative and perhaps even qualitative terms, when more realistic edge saturation and molecular size effects are introduced, and how this can affect carbon gasification kinetics (15), is the subject of our continued studies.

**Table 1a.** Comparison of C-C bond lengths (Å) in 2-ring model structures using B3LYP/6-31G(d)//HF/3-21G\* with Gaussian 98W.

|     | 1-2          | 2-3          | 3-4          | 4-10  | 5-10  | 5-6   | 6-7          | 7-8          | 8-9          | 1-9   |
|-----|--------------|--------------|--------------|-------|-------|-------|--------------|--------------|--------------|-------|
| N1  | 1.357        | 1.414        | 1.357        | 1.419 | 1.419 | 1.357 | 1.414        | 1.357        | 1.419        | 1.419 |
| N3a | 1.323        | <u>1.475</u> | <u>1.477</u> | 1.330 | 1.466 | 1.323 | <u>1.475</u> | <u>1.477</u> | 1.330        | 1.466 |
| N3b | <u>1.479</u> | <u>1.473</u> | 1.326        | 1.461 | 1.336 | 1.459 | 1.328        | <u>1.472</u> | <u>1.495</u> | 1.327 |

**Table 1b.** Comparison of atomic charges in 2-ring model structures using B3LYP/6-31G(d)//HF/3-21G\* with Gaussian 98W.

|     | C1    | C2   | C3    | C4    | C5    | C6    | C7    | C8    | C9    | C10   |
|-----|-------|------|-------|-------|-------|-------|-------|-------|-------|-------|
| N1  | -186  | -134 | -134  | -186  | -186  | -134  | -134  | -186  | .131  | .131  |
| N3a | -138  | -189 | .448  | -.305 | -.138 | -.189 | .448  | -.305 | .182  | .182  |
| N3b | -.190 | .503 | -.271 | -.169 | -.216 | -.219 | -.258 | .558  | -.163 | -.078 |

**Table 2a.** Comparison of C-C bond lengths (Å) in 4-ring model structures using B3LYP/6-31G(d)//HF/3-21G\* with Gaussian 98W.

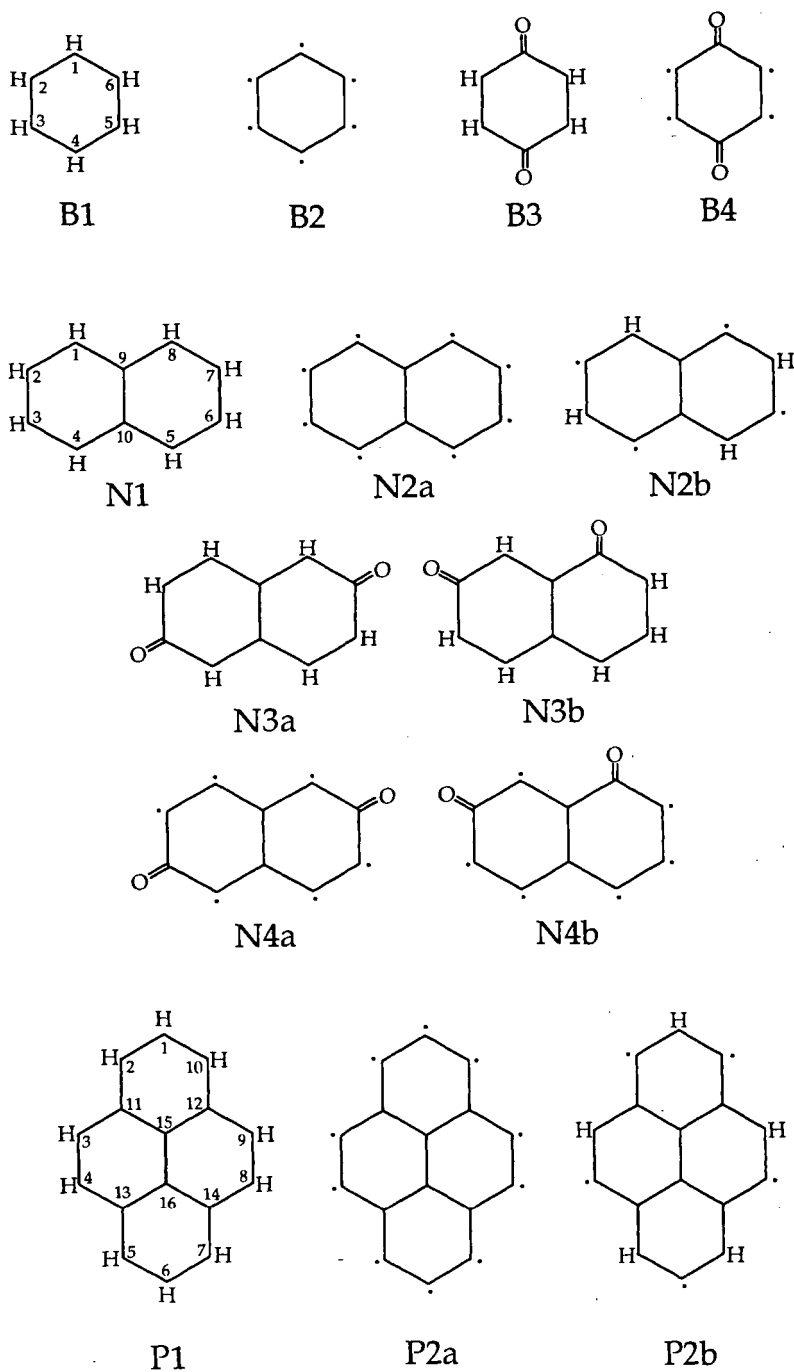
|     | 1-10         | 10-12 | 9-12         | 8-9          | 8-14         | 7-14         | 6-7          |
|-----|--------------|-------|--------------|--------------|--------------|--------------|--------------|
| P1  | 1.382        | 1.390 | 1.445        | 1.338        | 1.445        | 1.390        | 1.382        |
| P3a | 1.326        | 1.464 | 1.367        | 1.405        | 1.363        | <u>1.485</u> | <u>1.474</u> |
| P3b | 1.396        | 1.370 | <u>1.475</u> | <u>1.523</u> | <u>1.476</u> | 1.370        | 1.396        |
| P3c | <u>1.470</u> | 1.333 | 1.463        | 1.325        | 1.463        | 1.333        | <u>1.470</u> |

**Table 2b.** Comparison of atomic charges in 4-ring model structures using B3LYP/6-31G(d)//HF/3-21G\* with Gaussian 98W.

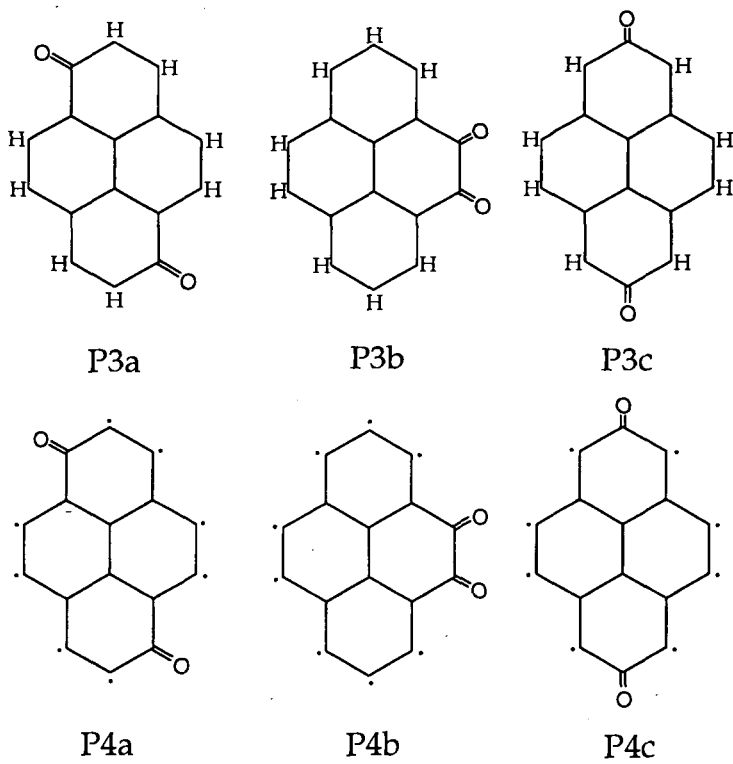
|     | C1            | C10           | C12   | C9            | C8            | C14   | C7            | C6            |
|-----|---------------|---------------|-------|---------------|---------------|-------|---------------|---------------|
| P1  | -0.119        | -0.230        | 0.161 | -0.186        | -0.186        | 0.161 | -0.230        | -0.119        |
| P3a | <u>-0.179</u> | <u>-0.157</u> | 0.167 | <u>-0.227</u> | <u>-0.185</u> | 0.048 | 0.390         | <u>-0.179</u> |
| P3b | <u>-0.121</u> | <u>-0.190</u> | 0.050 | 0.339         | 0.339         | 0.050 | <u>-0.190</u> | <u>-0.121</u> |
| P3c | 0.470         | <u>-0.343</u> | 0.238 | <u>-0.171</u> | <u>-0.171</u> | 0.238 | <u>-0.343</u> | 0.470         |

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**Figure 1.** Model structures selected to represent the important surface chemistry effects in carbon gasification kinetics.



**Figure 1 (continued).** Model structures selected to represent the important surface chemistry effects in carbon gasification kinetics.